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KINETICS OF STRAININDUCED CRYSTALLIZATION OF POLYMERS
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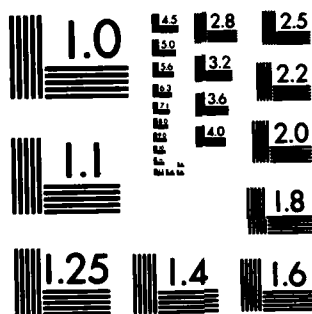
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KINETICS OF STRAIN-INDUCED CRYSTALLIZATION

OF POLYMERS DURING FLOW

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SUMMARY

The objectives were to measure the changes in crystallization rate (the primary objective), morphology and melting temperature of strain-crystallized polymers and to examine their origin(s) by comparing the results with various theoretical predictions.

Results from experimental studies of strain-crystallized polyethylenes, prepared in a simple shear couette rheometer, indicate a substantial increase in nucleation rate, a decrease in long period, as well as an increase in melting temperature with increasing shear. The changes appear to have the same thermodynamic origin in the reduction of the amount of melt entropy, $\Delta S'$, just prior to crystallization according to a strain-induced crystallization theory by Yeh and Hong. Consequently from the measured nucleation rate one can predict what the decrease in long period or the increase in melting temperature should be for a given strain-crystallized polyethylene. For example, the measured melting temperatures are indeed shown to be comparable to those predicted from nucleation rate measurements.

Among other significant findings are (1) higher molecular weight enhances the rate of strain-induced crystallization, in contrast to the usual retardation effect found under simple supercoolings and (2) the degree of c-axis orientation for strain-induced crystallites is always high ($f_c \geq 0.8$) when and if they form under shear. On the other hand, if shear-induced crystallization does not occur during shearing the oriented crystallites formed under simple supercooling conditions have comparatively low degree of c-axis orientation ($f_c \approx 0.2$).

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TECHNICAL REPORT

KINETICS OF STRAIN-INDUCED CRYSTALLIZATION OF POLYMERS DURING FLOW

Previously we have demonstrated that a simple shear field couette rheometer can be used to obtain nucleation induction times $t_i^{[1]}$ of strain-induced crystallites (SIC) and information about their nucleation rates $N^{[2]}$. The same couette rheometer was used to prepare numerous polyethylenes sheared at various temperatures and then quenched in ice water. Effects of shear rate $\dot{\gamma}$ and shearing temperature T_s on N (in terms of t_i), morphology (primarily in terms of c-axis orientation f_c and long period L) and melting temperature T_m were examined in detail. Extensive induction times were obtained on two different molecular weight polyethylenes to establish what effect, if any, molecular weight has on the nucleation rates of SIC.

Induction Time Analyses

First we were able to again confirm that the onset of an increase in shear force vs. time is an excellent indication of SIC (Fig. 1). For example, samples prepared at 135°C. show an induction time while those prepared at the same shear rate at 140°, 145° and 150° C. which do not strain-crystallize at such small supercoolings, do not show induction times. Melting temperature studies also confirm the absence of SIC crystallites in these Non-SIC samples with no induction times. WAXS studies, to be shown below, indicate that Non-SIC samples have much lower c-axis orientation ($f_c \approx 0.2$) than SIC samples which show induction times ($f_c \gtrsim 0.8$). This is an important finding in the case for shear-induced crystallization because for years many researchers believed that SIC crystallites, especially those formed by shear, could have a much wider range of f_c orientations because of the proposed row-nucleation model^[3]. This view has remained until now in spite of the fact that numerous experimental findings on

SIC from elongational strains have indicated otherwise^[4].

Analyses of induction times from numerous preparations (Figs. 2 and 3) all indicate that they follow an empirical equation $1/t_1 = A_1 \dot{\gamma} \exp(E_1/RT)$. The parameters A_1 and E_1 depend greatly upon molecular weight (Table 1). However they are independent of shear rate and temperature for SIC. Compared to thermally-induced crystallization^[5] the A_1 's are several orders larger and the E_1 's several times smaller. Since $1/t_1 = A_1 \dot{\gamma} \exp(E_1/RT) \exp(-\Delta F^*/RT)$, the variations in t_1 with molecular weight indicate (1) that the SIC nucleation rate increases with molecular weight, in contrast to thermally-induced crystallization where increasing molecular weight decreases the TIC nucleation rate and (2) that the origin of nucleation rate increase is primarily entropic, caused by a reduction in melt entropy, $\Delta S'$, which is contained in the expressions for ΔF^* ^[2]. According to our theory^[2], $\Delta S'$ is responsible for changes in nucleation rate, long period and melting temperature. Consequently one can show that from the known constants A_1 and E_1 (Table 1) we can predict the enhancements of nucleation-rate N^0/N (N^0 and N being the nucleation rates for SIC and TIC respectively) by equation 1, the equilibrium melting temperature T_m^0 for SIC by equation 2, and the critical nucleus thickness l_c^0 by equation 3 for a given molecular weight polyethylene.

$$\frac{N^0}{N} = \frac{A_1^0}{A_1} \dot{\gamma} \exp[(E_1^0 - E_1)/RT] = \frac{A_1^0}{A_1} \dot{\gamma} \exp(\Delta E_1/RT) \quad (1)$$

$$\frac{1}{T_m^0} = \frac{1}{T_m} - \frac{1}{T\Delta h} \left\{ \left[\frac{1}{\Delta f} - \frac{kT}{4b_0\sigma_s\sigma_e} \left(\ln\left(\frac{A_1^0}{A_1}\right) + \ln(\dot{\gamma}) + \frac{\Delta E_1}{RT} \right) \right]^{-1} - \Delta f \right\} \quad (2)$$

$$l_c^0 = l_c - \frac{kT}{4b_0\sigma_s\sigma_e} \left[\ln\left(\frac{A_1^0}{A_1}\right) + \ln(\dot{\gamma}) + \frac{\Delta E_1}{RT} \right] \quad (3)$$

The three equations were derived on the assumption that the SIC process is heterogeneous. Otherwise another set of equations can be derived.

Morphological Studies

From WAXS we were able to obtain orientation functions f_a , f_b and f_c for both SIC and Non-SIC samples. All SIC samples are found to have relatively high f_c values. For example, of all the samples shown in Figure 4a (Fig. 4^[7]) which were sheared at 6.5 sec^{-1} for the same amount of shear, the only one that has an induction time and high f_c value is the one sheared at 135°C . All the other samples in Figs. 4a and 4b show no t_i and relatively low f_c values because they do not contain SIC crystals.

It is also of interest to note that the SIC samples contain an additional triclinic crystal phase as indicated by the presence of the "extra" reflections (Fig. 5). These "extra" reflections have been indexed to correspond to a triclinic phase (Figure 6), which results from strain-induced crystallization during flow^[8].

From SAXS studies we were able to ascertain the presence of two long periods, L_1 and L_2 (Figure 7^[9]). L_1 (~50-60 nm) varies with shearing conditions, $\dot{\gamma}$ and T_s , indicating that it corresponds to the SIC crystals formed at the shearing temperature. L_2 (~30 nm) remains essentially unchanged with $\dot{\gamma}$ and T_s , indicating that L_2 corresponds to crystals formed during TIC, i.e. during the quenching process at low temperatures.

The decrease of L_1 with $\dot{\gamma}$ arises from the decrease in melt entropy ΔS ^[2] with increase in $\dot{\gamma}$ and can be predicted from equation 3. The slight difference in long periods L_2 (32 nm vs. 30 nm) shown in Figure 7 is real; however the origin of this difference is unclear at the present time.

Melting Temperature

Melting temperatures were obtained under equilibrium conditions using

restrained samples in DSC. Double peaks in DSC endotherms $T_{m,h}$ (136-148°C.) and $T_{m,l}$ (131° C.) were observed for all the sheared samples with induction times. However only $T_{m,l}$ was observed for Non-SIC samples, which showed no induction time. $T_{m,h}$ varied while $T_{m,l}$ remained essentially constant with $\dot{\gamma}$ and T_g , again indicating that $T_{m,h}$ can be associated with SIC crystals generated during the shearing process and that $T_{m,l}$ can be associated with thermally-induced crystallites generated during the quenching process. The measured T_m results are shown in Figure 8, together with melting temperatures predicted from equation 3. The agreement is considered to be quite good considering the predicted melting temperatures are equilibrium values for infinitely large crystals whereas the measured melting temperatures were from crystallites of limited crystal thicknesses (<50-60 nm from Fig. 7).

We can conclude by saying that although there are still numerous unresolved questions regarding SIC, the present study has clarified several important controversial aspects, namely, (1) the degree of orientation of SIC crystals, (2) the magnitude of changes in crystallization rate, long period and melting temperature of SIC polymer and (3) the origin of their changes. We hope that these aspects will become less controversial as our results become better known and substantiated by other researchers.

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Table 1

Parameters A_1 (sec^{-1}) and E_1 (Kcal/mole).

<u>Polymer</u>	<u>\bar{M}_w</u>	<u>A_1</u>	<u>E_1</u>
Marlex 6050	90,000	2.4×10^{-226} [5]	440 [5]
Marlex 6050	90,000	8.3×10^{-123}	220
Marlex 6001	200,000	1.2×10^{-24}	41.4

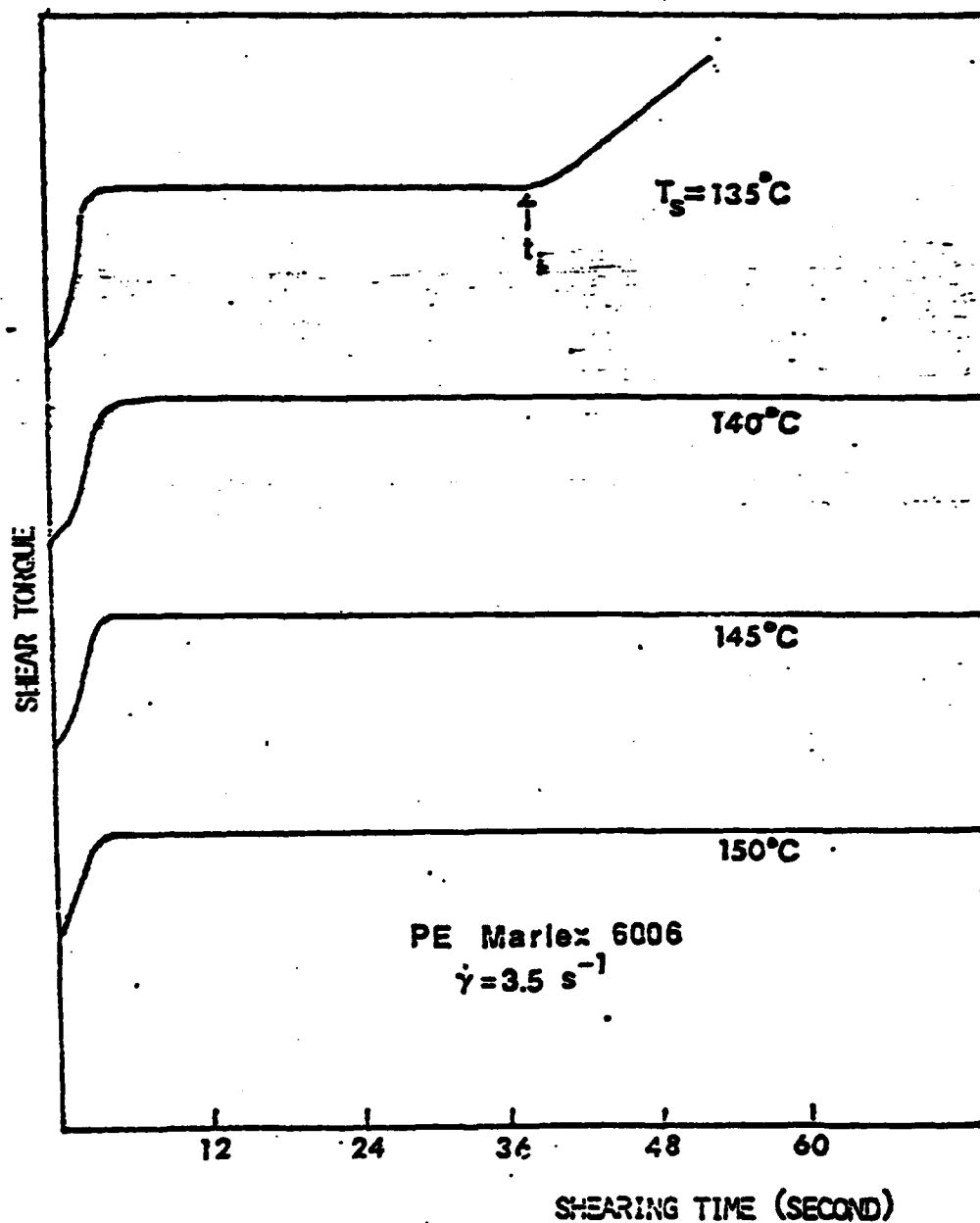


Figure 1 Polyethylenes sheared at various T_s showing the presence or absence of induction time, t_1 .

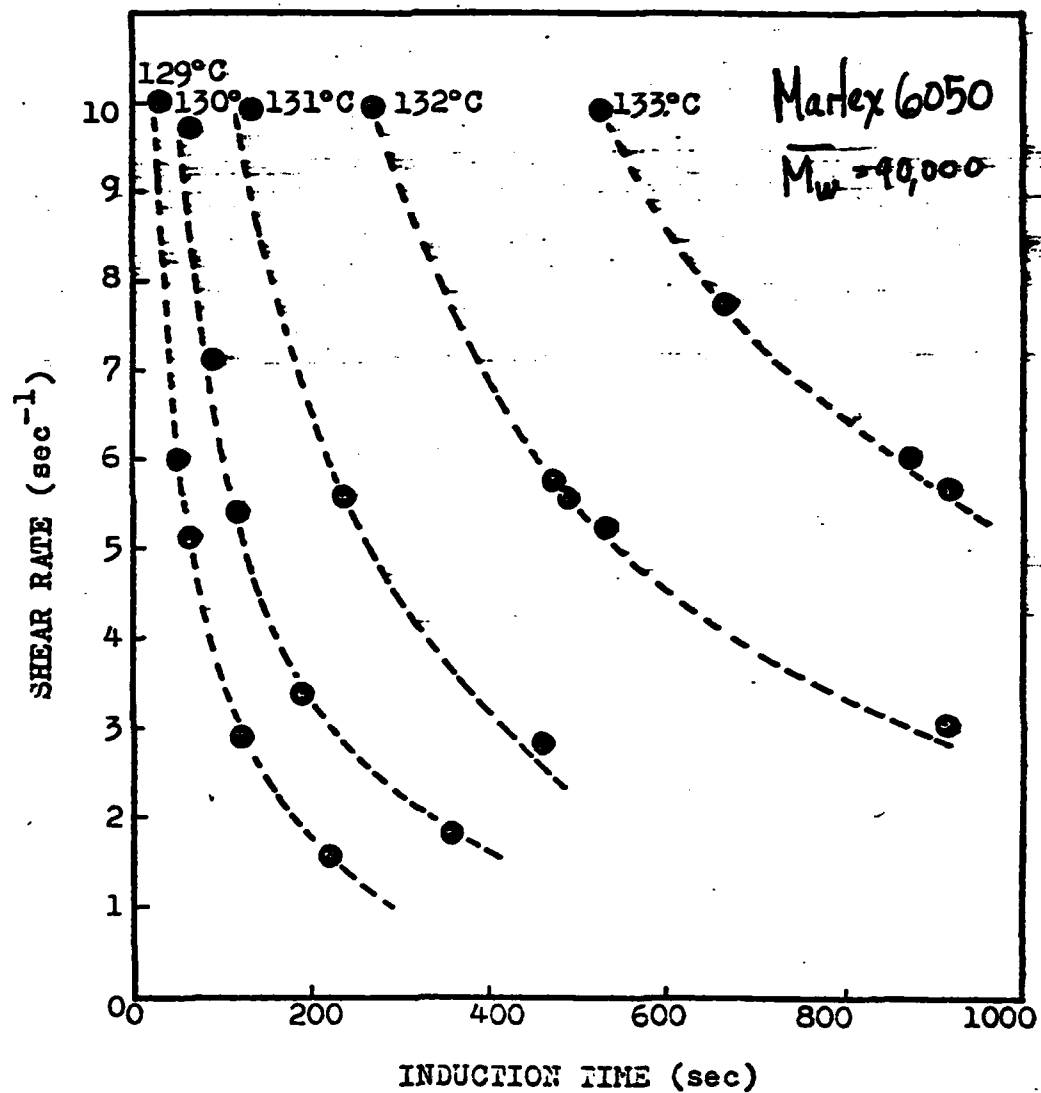


Figure 2. Shear rate as a function of induction time for polyethylene sheared at constant temperatures.

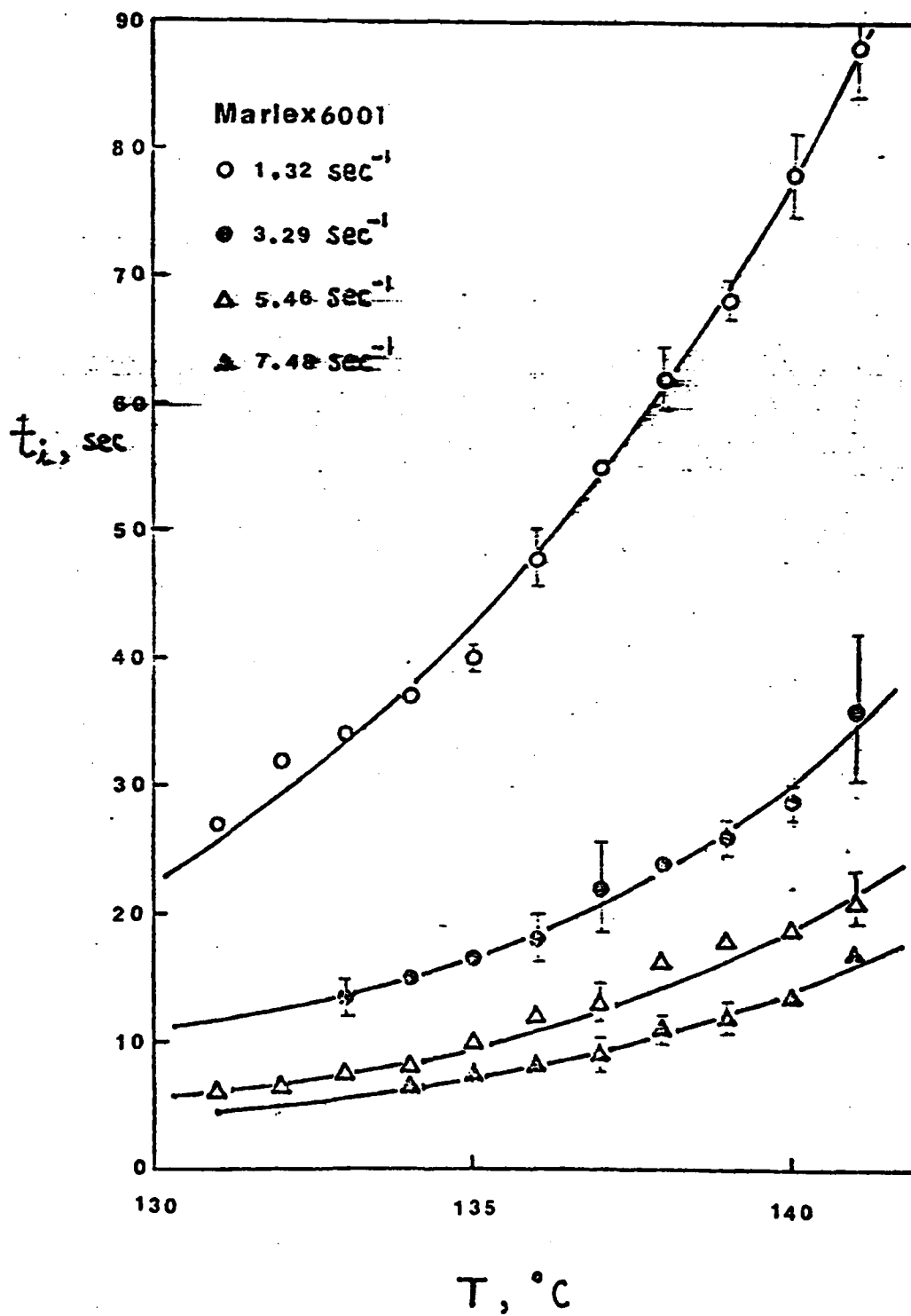


Figure 3. Effects of shear rate and temperature on induction time of PE Marlex 6001 (M_w - 200,000).

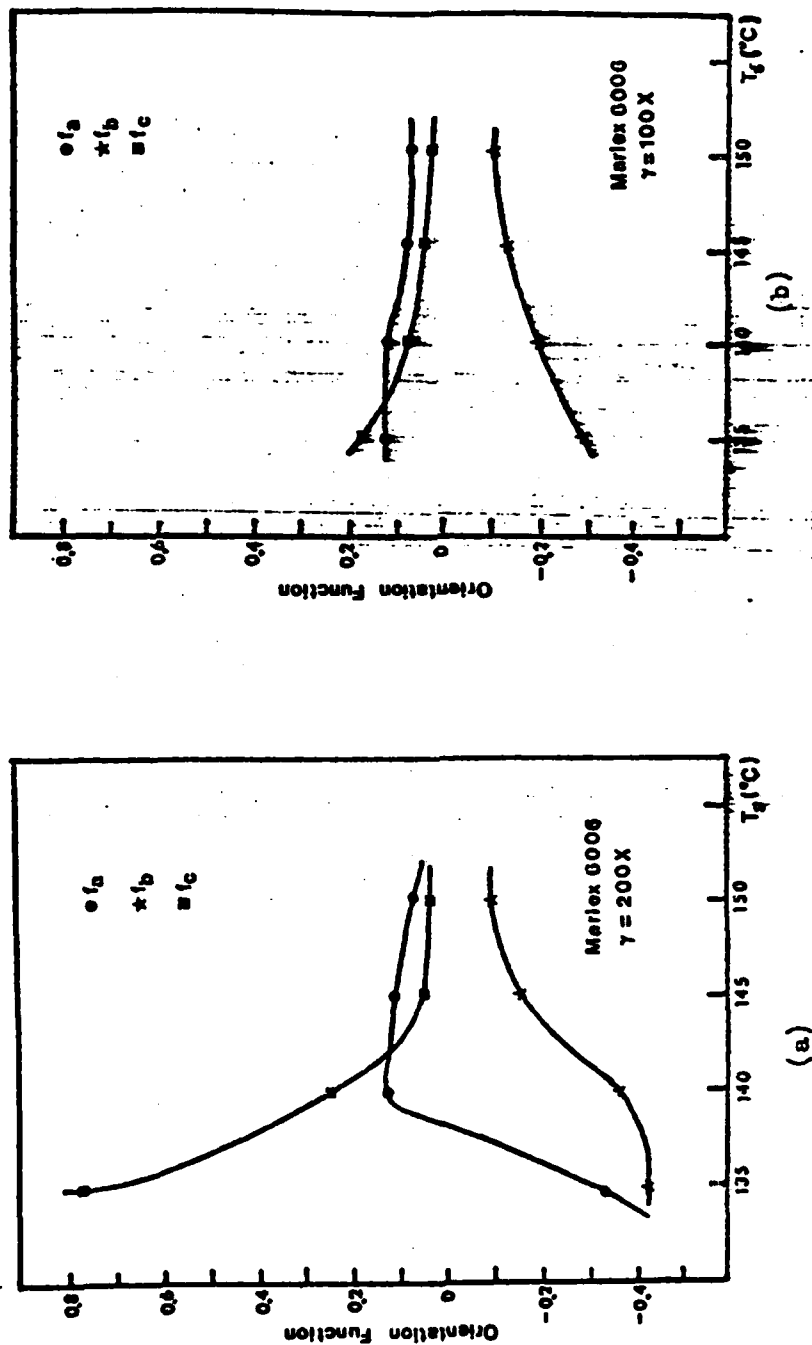


Figure 4. Effect of shearing temperature, T_g , on orientation functions, f_a , f_b , f_c .

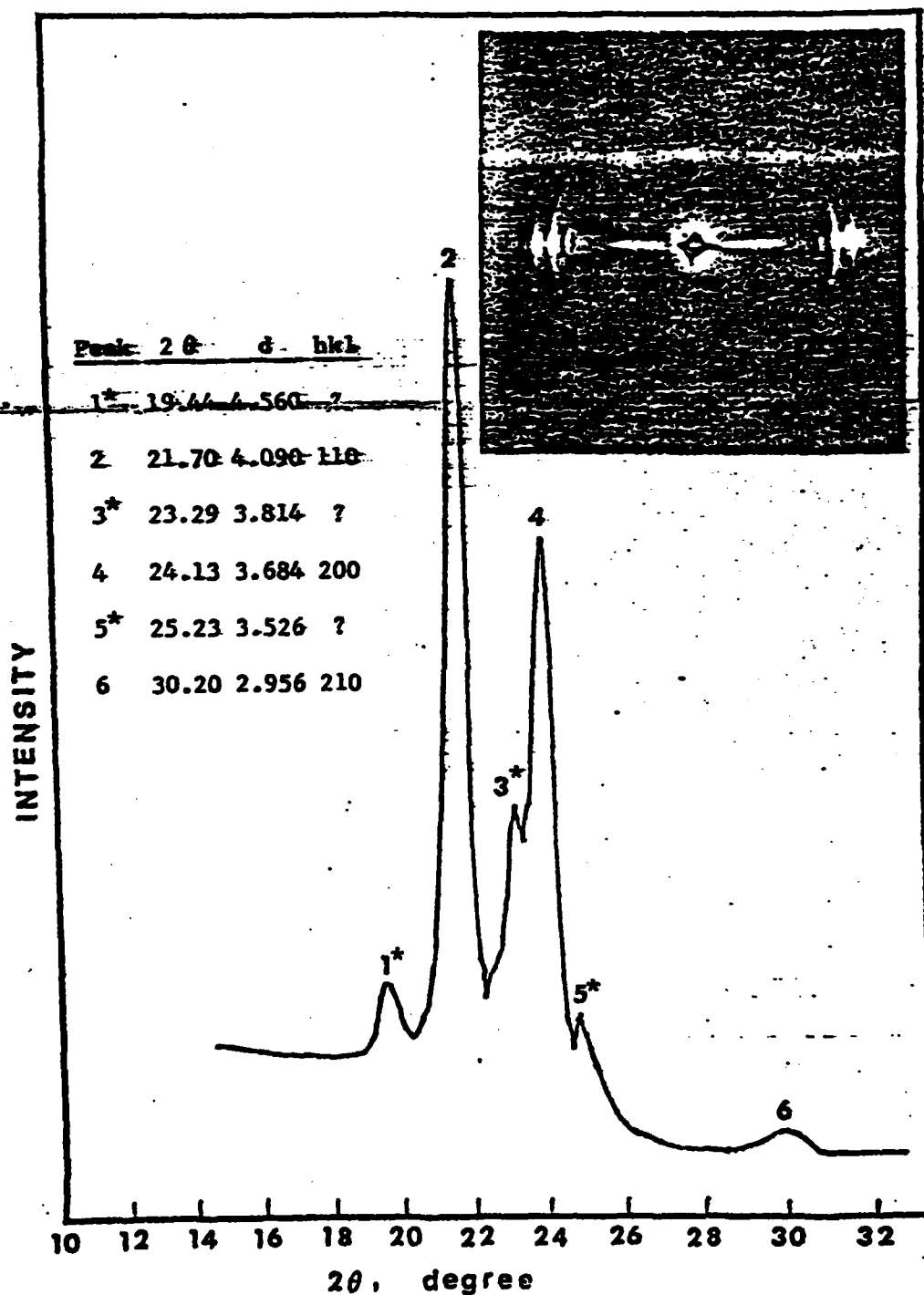


Figure 5. Wide-angle X-ray scattering pattern and equatorial scan of strain-crystallized polyethylene. * indicates "extra" reflections. Incident beam is in z-direction.

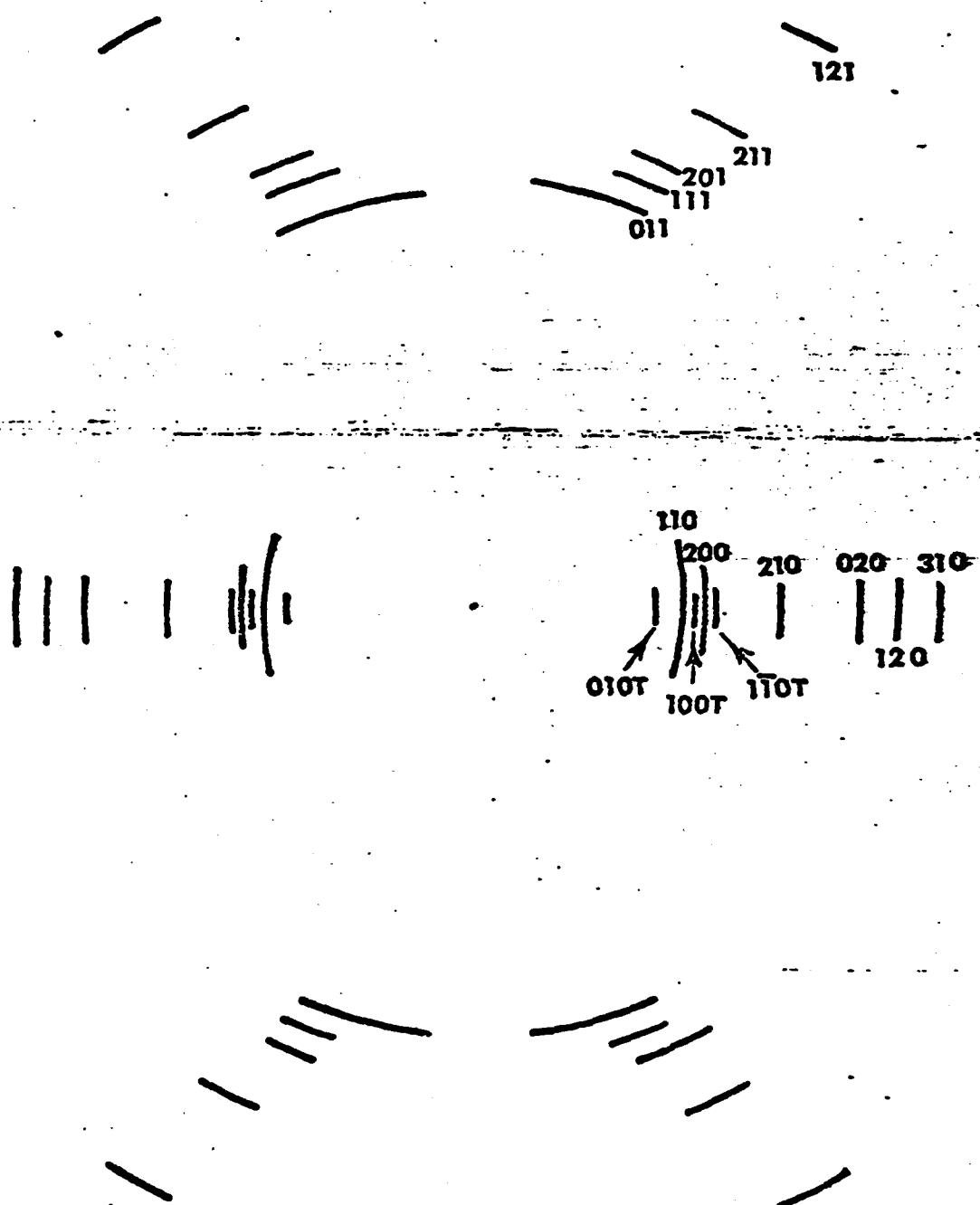


Figure 6. Schematic representation of the indexed X-ray diffraction pattern of strain-crystallized polyethylene. Triclinic reflections are indicated by arrows.

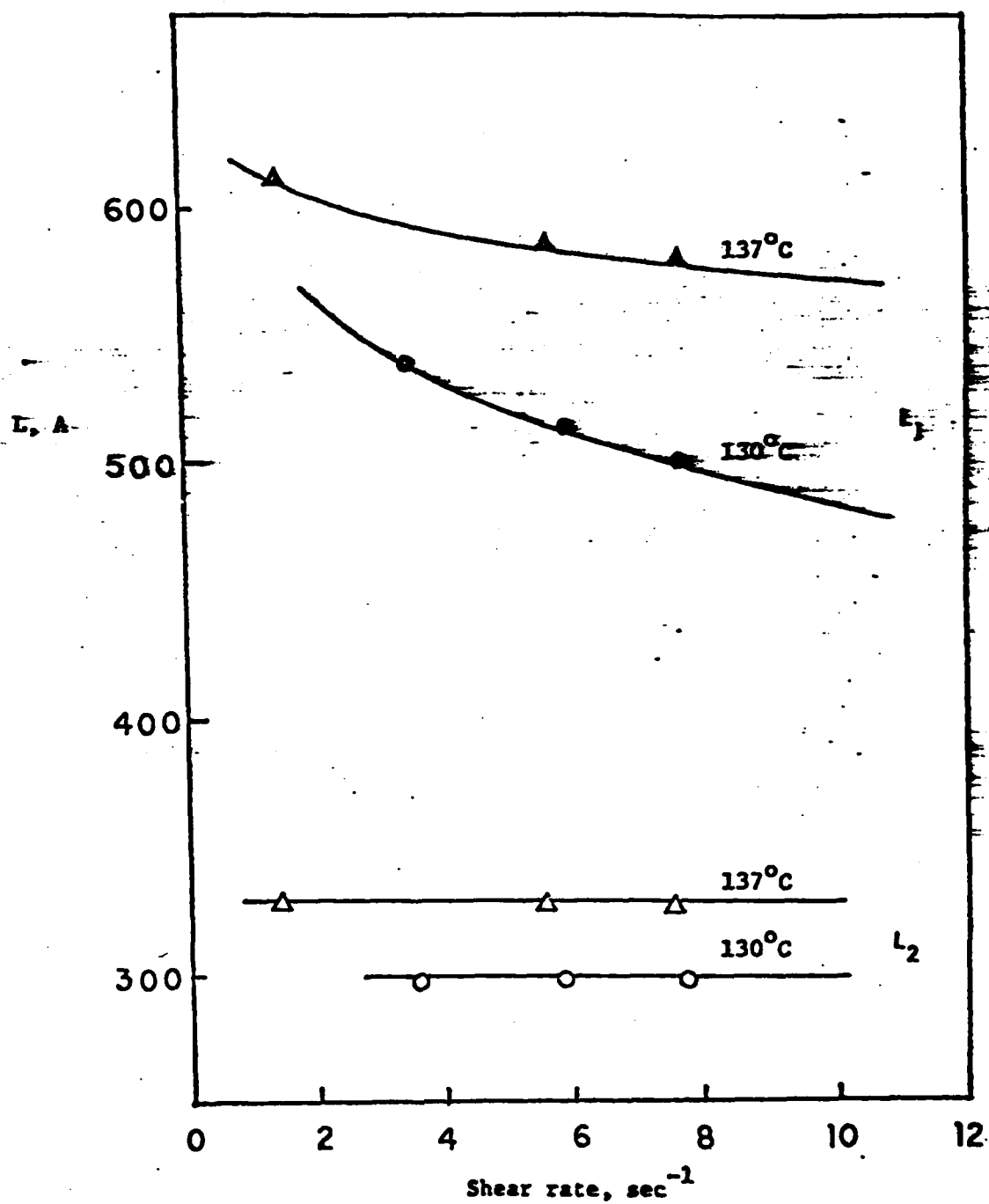


Figure 7. Effect of shear rate on long period of strain-crystallized PE prepared at 130°C . and 137°C .

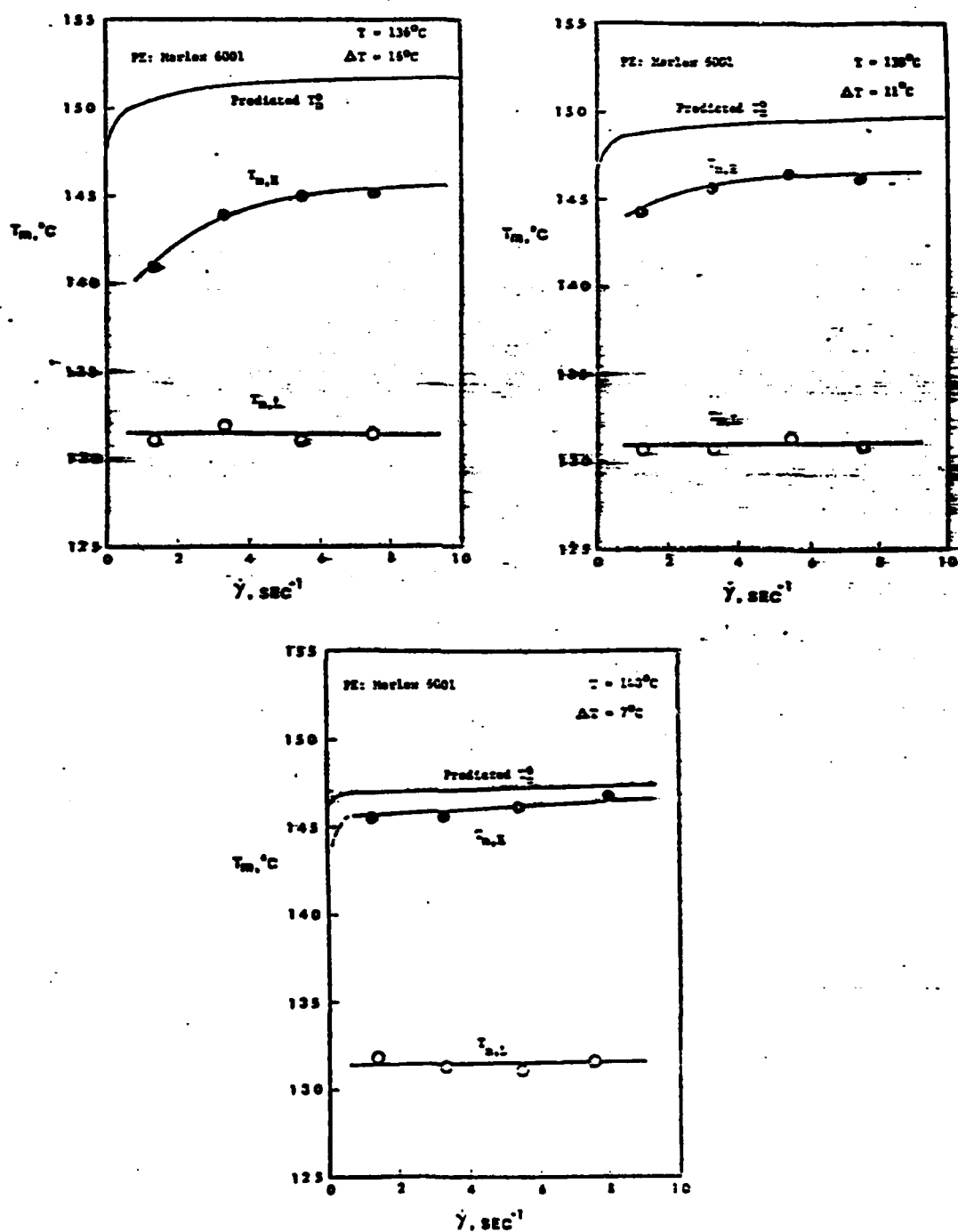


Figure 8. Comparisons of measured $T_{m,h}$ and $T_{m,l}$ with predicted T_m^0 as a function of shear rate for PE crystallized at 136°C .

Publications and Presentations

1. Equilibrium Melting Temperature of Strain-Crystallized Polymers, K.Z. Hong and G.S.Y. Yeh, Bull. APS 24(3), 376 (1979).
2. Melting Behavior of Strain-Crystallized Polyethylenes, K.Z. Hong and G.S.Y. Yeh, Bull. APS 25(3), 316 (1980).
3. Effects of Shear Rate and Crystallization Temperature on Long Period of Polyethylene Crystallized Under Controlled Shear, G.S.Y. Yeh and J. Haase, Bull. APS 27(3), 260 (1982).
4. Morphology and Thermal Behavior of Shear-Crystallized Polyethylene, G.S.Y. Yeh, Main Invited Lecture at the 14th Europhysics Conference on Macromol. Physics (Abstract attached, Appendix I).
5. Effects of Shearing Conditions on Crystalline Orientation and Relaxation in Polyethylene, E.S. Hsiao, R.E. Robertson and G.S.Y. Yeh, Polymer Engineering and Sci., Accepted for Publication (Abstract attached, Appendix II).

Appendix I

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MORPHOLOGY AND THERMAL BEHAVIOR OF SHEAR-CRYSTALLIZED POLYETHYLENE

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The long-period and melting temperatures of polyethylene, shear-crystallized in a Cosette apparatus at various shearing temperatures T_g (110-143°C) and rates $\dot{\gamma}$ (1.12-7.48 sec⁻¹) and then quenched in ice-water, were measured and compared with predicted values according to the strain-induced crystallization theory (SIC) of Yeh and Rong (Polymer Eng. and Sci., 19, 395 (1979)).

SAXS and DSC data showed the presence of two long periods, L_1 and L_2 , and two melting temperatures, $T_{m,h}$ and $T_{m,l}$. L_1 (~50-60 nm) and $T_{m,h}$ (~116-148°C) varied while L_2 (~30 nm) and $T_{m,l}$ (~131°C) remained essentially unchanged with T_g and $\dot{\gamma}$, indicating that L_1 and $T_{m,h}$ are associated with SIC crystals generated during the shearing crystallization process and that L_2 and $T_{m,l}$ associated with thermally-induced crystallites generated during quenching. Furthermore the results showed that L_1 decreased with $\dot{\gamma}$ and increased with T_g and $T_{m,h}$ increased with both $\dot{\gamma}$ and T_g in a manner as expected from the reduction in melt entropy $\Delta S'$. Therefore L_1 can be calculated from measured $T_{m,h}$ or vice versa. Values of L_1 thus calculated are found to be in reasonably good agreement with those determined from SAXS.

14 Europhysics Conference on Macromol. Physics
66, 94 (1982)

Appendix II

Effects of shearing conditions on crystalline orientation and relaxation in polyethylene

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Oct 14, 1982.

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ABSTRACT

The effects of shearing conditions (i.e., shear temperature and shear rate) on the degree of orientation of polyethylene Marlex 6006 and to what extent the induced orientation could be relaxed were examined in this study.

Two types of samples were prepared; namely, SIC and non-SIC samples. The SIC samples show induction times and possess a high degree of C-axis orientation along the shear direction. The induced orientation of SIC samples can be relaxed to a small extent but does not reach a steady value. Non-SIC samples do not show induction times and they show low degrees of C-axis orientation. The induced orientation of non-SIC samples can be relaxed to a steady state value with an activation energy of 90 kJ/mole.

Our results also indicate that when the shear temperature is at and above 145°C, polyethylene can be sheared up to 200X without introducing any significant molecular orientation even at very high shear rates.

Appendix III

List of Participating Personnel

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1. G.S.Y. Yeh, Principal Investigator
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3. T. Lin, MS, 1982
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6. J. Capo
7. R. Van Druen

